Diradicaloids: Description by the Spin-Restricted, Ensemble-Referenced Kohn−Sham Density Functional Method

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A Kohn−Sham-type computational scheme capable of treating systems with strong nondynamic correlation is presented. The scheme, dubbed the spin-restricted, ensemble-referenced Kohn−Sham (REKS) method, is based on the representation of the density and energy for a strongly correlated system as weighted sums of densities and energies of several Kohn−Sham (KS) determinants. An optimal set of orthonormal KS orbitals and occupation numbers is obtained by minimizing the ground-state energy as a function of the density. Results of REKS calculations are reported and cover the following chemically important situations: (1) avoided crossing of potential energy surfaces, (2) bond-breaking processes, and (3) electronic structure of diradicals. The results of REKS calculations are compared with the available Kohn−Sham solutions for cases in which the exact density is known, as well as with results of conventional multireference ab initio methods and with the currently available density functional approaches.

I. Introduction

Density functional theory (DFT) is applied in quantum chemistry almost exclusively via the Kohn−Sham (KS) method.[1] With existing density functionals, the KS method successfully describes molecular systems for which the dynamic electron correlation dominates the total correlation energy.[2] However, the conventional KS calculations are much less reliable for states with strong nondynamic correlation.[3−5] Strong nondynamic correlation is ubiquitous and appears in bond-breaking processes, in bond rearrangements at transition points (avoided crossing situations), in fractionally occupied degenerate electronic configurations (e.g., in diradicals), in many excited states, etc.

The extension of DFT to states with strong nondynamic correlation is nowadays an active field of research. Most of the approaches[6−10] are hybrids of the conventional multireference (MR) treatments[11,12] with the KS method. A crucial problem for such hybrid MR/DFT schemes is the "double-counting" of correlation energy[9] which results in serious deviations from the conventional KS calculations. As a result, this may require the development of density functionals tailored for a desired problem[9] or an introduction of the empirical parameters,[10] and hence an eventual standardization of the density functional calculations may be difficult to achieve.

The symmetry-broken, spin-unrestricted KS (UKS) approach[13] is frequently used to simulate nondynamic correlation.[14−18] However, this approach suffers from heavy spin contamination that can make identification of electronic states difficult (in some cases even impossible). Even worse, sometimes the UKS method may lead to prediction of wrong ground states of species with strong correlation and also to prediction of wrong pathways of chemical reactions. Thus, it seems desirable to extend the KS method to strongly correlated systems in a more or less consistent way and develop a computational scheme free of the above deficiencies. Such a scheme may be considered as a density functional analogue of the conventional multireference methods that is free of the double counting of the correlation energy.

The basic Ansatz of the Kohn−Sham method[1] in DFT is the representation of the ground-state density of a real many-electron system by the ground-state density of a fictitious system of noninteracting particles. Conventionally, the density of such a noninteracting state is described by a single KS determinant. The ground-state energy of the real system can then be found from the known density,[19] which is easily obtained by use of KS orbitals. Thus, the representability of the density of a real many-electron system by a single determinant which is the ground state of a certain noninteracting system is the crucial and foremost condition for the success of the KS method.[4,5,20] From procedures based on first principles, it has been computationally demonstrated[4,21−23] that in many simple cases, such as noble gas atoms, diatomic molecules H_2, LiH, and N_2, there exists such a noninteracting Kohn−Sham reference system. However, in situations typified by strong nondynamic correlation, the same procedure failed to fit the density to a single Kohn−Sham determinant unless degenerate, or nearly so, orbitals were taken with fractional occupation numbers (FONs).[4,5] To be physically founded, these fractional occupation numbers must follow from ensemble averaging.[20,24,25] Thus, the density of strongly correlated systems which require FONs is in fact a weighted sum (ensemble) of densities of several single KS determinants.[4,5]

At first glance, what remains is to insert the ensemble density (alternatively, density with fractional occupation numbers) into existing density functionals. However, such a scheme, known as DFT−FON,[26−29] is less successful in calculation of strongly correlated systems[5] than is the usual DFT procedure in its application to "normal" systems (i.e., systems in which the nondynamic correlation is weak and the dynamic one prevails). Indeed, arguments have been given[5,30,31] for the exclusive use of the existing density functionals with single-determinant densities, because only in such a representation do they comply

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with the important sum rules for the exchange and correlation holes and the on-top hole densities.[32]

Fractionally occupied natural orbitals can be obtained from the symmetry-broken UKS (or UHF) one-electron density matrices. In principle, these fractional occupations could also have been regarded as nascent from an ensemble density. However, the UKS energy depends not only on the density, represented with FONs, but also on an unphysical spin density, and consequently the symmetry-broken, spin-unrestricted approach cannot be regarded as a KS method with a proper ensemble density representation.

An alternative derivation of new density functionals that concur with the formal properties of the ensemble densities must be sought. Such an approach could be based on the representation of the ground-state energy of strongly correlated systems in a form of a weighted sum of energies of several KS determinants,[5,30,31] in a manner that obeys spatial and spin symmetry. In recent papers[33,34] we employed such a representation to develop a spin-restricted Kohn−Sham method capable of treating the systems in which the strong nondynamic correlation is symmetry-dictated, as is the case in multiplet states. Subsequently,[35] this scheme was couched in a fully variational form to handle situations with a symmetry-independent nondynamic correlation appearing in diradicaloid species. The scheme, termed the spin-restricted, ensemble-referenced Kohn−Sham (REKS) method, was tested in calculations for a number of diradicaloid species[35] and later was successfully applied to study the intersystem crossing in small-ring alkenes[36] and the states of tetramethyleneethane (TME) diradical.[37] Unlike the combinations of the multireference methods with DFT, the REKS method is free of double-counting of the correlation energy and, without any empirical parameters, reproduces results of the conventional KS calculations with any existing density functional. Furthermore, the REKS method is free of spin contamination.

In the present paper we report a systematic comparison of the REKS method with the usual density functional approaches in the calculation of a wide range of chemically important situations with strong nondynamic correlation, such as: (1) avoided crossing of potential energy surfaces, (2) bond-breaking processes, and (3) electronic structure of diradicals. The results of the REKS and the standard density functional calculations will be compared with the available, essentially accurate Kohn−Sham solutions[5] and with the results from the conventional multireference ab initio methods. These comparisons should serve as a validation of the REKS method in applied quantum chemistry.

The paper is organized as follows: In Section II we sketch the derivation of the REKS method and outline the ideas that may be used for extending this method beyond the diradicaloid situations. Section III describes details of the calculations undertaken in the present paper. In Section IV the results of the calculations with REKS, as well as with the usual single-determinant KS method (RKS) and with the symmetry-broken, spin-unrestricted KS (UKS) method, are be compared against results of the multireference (CASSCF, CASMP2, MR−(S)DCI) ab initio calculations. Section V concludes the paper.

II. REKS Method

The present version of REKS is suited for singlet states where two electrons share two degenerate or nearly degenerate orbitals, as occurs in singlet diradicals. The method is based on the representation of the density and energy for a strongly correlated system as weighted sums of degenerate or quasidegenerate single Kohn−Sham (KS) determinants. The weighting factors in the weighted sum representation are associated with the FONs of the KS orbitals from which the single KS determinants are constructed.[25]

The density representation is straightforward. In terms of the KS orbitals and fractional occupation numbers, it is given by eq 1:[35]

$$\rho_{\text{gs}}(\mathbf{r}) = \sum_{k\in\text{core}} 2|\phi_k(\mathbf{r})|^2 + n_r|\phi_r(\mathbf{r})|^2 + n_s|\phi_s(\mathbf{r})|^2 \tag{1}$$

where n_r and n_s are the fractional occupation numbers of “active” orbitals ϕ_r and ϕ_s which share the electron pair, and ϕ_k are the doubly occupied, closed-shell core orbitals. Thus, the density depends explicitly on the KS orbitals and FONs. Hence, the energy expression which is to be minimized with respect to the density, eq 1, should be constructed to depend on the KS orbitals and FONs only.

To express the ground-state energy of a strongly correlated system as a weighted sum of single-determinant KS energies with weighting factors depending on the FONs only, we considered for the given case the 2 × 2 secular problem in the basis of the symmetry-adapted diabatic states, eqs 2 and 3.

$$\Psi_{\text{cov}} = \frac{1}{\sqrt{2}}(|\phi_r\bar{\phi}_r| - |\phi_s\bar{\phi}_s|) \tag{2}$$

$$\Psi_{\text{ion}} = \frac{1}{\sqrt{2}}(|\phi_r\bar{\phi}_r| + |\phi_s\bar{\phi}_s|) \tag{3}$$

These states are the pure-spin and spatial-symmetry singlet states, covalent and ionic, of a noninteracting system where the two orbitals ϕ_r and ϕ_s are degenerate by symmetry (e.g., 90°-twisted ethylene).[34,35] The energies of these diabatic states may be derived from the symmetry reasoning[30,31] and represented as sums of single-determinant KS energies.[34,35] Furthermore, the coupling matrix element of the interacting Hamiltonian between the diabatic states is given by the difference of energies of two single KS determinants and does not require elements of the $r_{12}{}^{-1}$-operator between the diabatic states as in the configurational interaction (CI) method.[34,35] It is an advantage of using the symmetry-adapted diabatic states instead of single KS determinants that all matrix elements in the corresponding problem may be represented in terms of single-determinant energies. Moreover, the symmetry adaptation helps also in more complicated cases which cover more “active” orbitals and “active” electrons.[38]

Resolving the aforementioned secular problem for the lowest energy state, and imposing a requirement that the resulting energy formula should reproduce the conventional single-determinant KS calculation as closely as possible, we arrived at the expression for the ground-state energy in the REKS method, eq 4.[35]

$$E_{\text{gs}}^{\text{REKS}} = \frac{n_r}{2}E(\phi_r\bar{\phi}_r) + \frac{n_s}{2}E(\phi_s\bar{\phi}_s) + (n_rn_s)^{3/4}\Big[E(\phi_r\phi_s) - \frac{1}{2}E(\phi_r\bar{\phi}_s) - \frac{1}{2}E(\phi_s\bar{\phi}_r)\Big] \tag{4}$$

In eq 4 $E(\phi_r\bar{\phi}_s)$ denotes the KS energy of the single-determinant $|...\phi_r\bar{\phi}_s\rangle$. Note that the ground-state energy of a system with strong nondynamic correlation is represented in terms of the fractional occupation numbers of KS orbitals and the density functional energies of single KS determinants only. Precisely the same expression holds also for the ground-state density, with the single-determinant energies in eq 4 replaced by the densities of single KS determinants. It is easy to see that such a density reduces to density with FONs (eq 1).

The one-electron orbitals and fractional occupation numbers are obtained in the REKS method self-consistently by minimizing the energy (eq 4) with respect to the density (eq 1). Because the REKS ground-state energy (eq 4) is not an explicit functional of the density (eq 1) its functional derivative is not easily evaluated. Thus, a self-consistent implementation of the Kohn−Sham method may require construction of the multiplicative KS potential from the orbitals by the optimized effective potential method.[39] However, such a procedure seems rather impractical in molecular calculations, and in implementation of the self-consistent REKS calculations we stick to an alternative approach[40] widely used in DFT when dealing with orbital-dependent and hybrid density functionals. In this case, the energy is minimized with respect to the orbitals (under constraint of orthonormality) and construction of the multiplicative KS potential is abandoned.[40] Further details of the REKS implementation may be found in ref 35.

Important features of the REKS method are as follows: (1) It can be used together with any existing density functional. (2) It enables one to describe states of pure spin and spatial symmetry (unlike the spin-unrestricted method). (3) For systems without strong nondynamic correlation, it yields virtually the same energies (within a fraction of mhartree) as conventional density functional calculations.

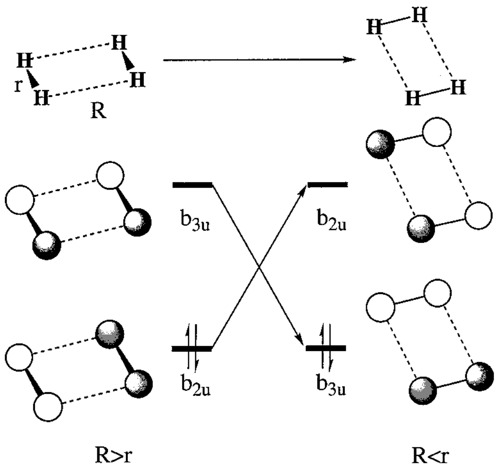
In its present form, REKS applies to singlet states with two “active” electrons in two “active” orbitals, and by analogy with CASSCF may be termed REKS(2,2) (i.e., two “active” electrons in two “active” orbitals). However, the REKS method can be extended for other chemically important situations, with more “active” electrons and “active” orbitals. For instance, considering a symmetry-adapted 3 × 3 secular problem for model systems with three electrons in three orbitals, such as doublet states of triradicals (e.g., $^2B_1$ term of 90°-twisted σ cation-radical of ethylene), it is possible to derive an energy expression for the strongly correlated low-spin state, i.e. energy formula of the REKS(3,3) method. The same work can also be performed for situations with four electrons in three orbitals, like in the ground singlet state of the C_2 molecule,[4] and with two electrons in three orbitals (i.e., the REKS(4,3) and REKS(2,3) methods). However, the self-consistent calculations using these methods are not as yet implemented and will be deferred for subsequent papers.[38] In the present paper, we concentrate on a systematic comparison of the current version REKS(2,2) with the standard density functional methods, the single-determinant KS (RKS) method, and the symmetry-broken, spin-unrestricted KS (UKS) method.

III. Details of Calculations

The REKS method has been implemented in the CADPAC5 quantum-chemical package.[41] The self-consistent calculations as well as the analytical gradients are available. The analytic second derivatives are not implemented. Because the numeric calculations of the second derivatives are quite inefficient, we calculated frequencies only in a few cases, mostly to characterize the saddle points.

All REKS and RKS calculations and most of the UKS calculations reported have been performed using the CADPAC5 program. Because the one-electron orbitals in the REKS and RKS methods are symmetry-adapted, these calculations explore the molecular symmetry at a full scale. To obtain the natural orbitals from the symmetry-broken solutions, some UKS calculations have been performed using the GAUSSIAN98 package.[42] The UKS calculations have been performed with symmetry switched off.

SCHEME 1



The conventional ab initio calculations reported have been performed using the CADPAC5 and GAUSSIAN98 programs for the single-reference methods, RHF and QCISD(T). The UHF and multireference CASSCF[11] and CASMP2[43] calculations have been performed using the GAMESS−US package.[44]

All calculations employ basis sets with the Cartesian d- and f-functions. The basis sets are the cc-pV5Z basis set[45] modified as suggested in ref 5, the TZ2P basis set,[41,46] and the 6-31G* basis set.[47]

IV. Results and Discussion

(a) Chemical Situations of Avoided Crossing. We begin our consideration with the symmetry-forbidden four-center exchange reaction $H_2 + H_2$. The potential energy surface (PES) of this reaction has been studied[5] with the help of the extensive MR−(S)DCI calculations in a large quintuple-zeta basis set (cc-pV5Z). The essentially accurate ensemble KS solutions around the square D_{4h} symmetric transition state have then been constructed from the ab initio densities.[5] Along the rectangular reaction mode presented in Scheme 1, the b_{2u} (in D_{2h}) orbital, initially doubly occupied, becomes vacant in the products, while the initially empty b_{3u} orbital gets filled. As the transition state is approached, the strong correlation due to near-degeneracy sets in, and the exact KS solution in this region corresponds to an ensemble of the two KS determinants, one with doubly occupied b_{2u} orbital and another with the doubly occupied b_{3u} orbital, thus leading to fractional occupation numbers of these orbitals. The exact FONs of the KS orbitals have been determined for a number of points along the reaction path.[5] The DFT−FON[26−29] calculations employing the same large basis set and different density functionals have been performed,[5] and their results are available for comparison with REKS.

In the present paper we performed calculations for a number of points along the reaction path considered in ref 5 using the REKS, RKS, and UKS methods. All calculations employ the same basis set used in ref 5 and the BLYP[48] density functional. In Table 1 and Figures 1 and 2, the results of our calculations are compared with the available literature data. The comparison of the FONs of the KS orbitals generated by the REKS, DFT−FON, and UKS[49] methods against the exact numbers (given in the KS/CI column of Table 1) reveals that the REKS method describes the ensemble KS solution better than the other methods. It should be noted that the REKS occupation numbers are not sensitive to the type of functional and remain essentially

TABLE 1: MR−(S)DCI Energies and Exact KS Fractional Occupation Numbers Compared with Results of REKS/BLYP, RKS/BLYP, DFT-FON/BLYP and UKS/BLYP and (4,4)CASSCF Calculations for the Symmetry-forbidden $H_2 + H_2$ Reaction

		n^c					ΔE^d					
R^a	r^b	KS/CI^e	REKS^f	DFT-FON^g	UKS^{f,h}	CASSCF^{f,h}	KS/CI^e	REKS^f	DFT-FON^g	RKS^f	UKS^f	CASSCF^f
2.32	2.32	1.00	1.00	1.00	1.00	1.00	147.5	149.6	163.2	167.8	135.1	143.1
2.35	2.29	1.36	1.27	1.80	1.11	1.26	146.2	148.7	160.2	160.6	134.7	142.2
2.40	2.21	1.86	1.72	2.00	1.36	1.65	138.7	141.1	145.4	145.1	131.4	134.9
2.50	2.06	2.00	1.97	2.00	1.83	1.86	114.2	115.8	116.1	118.3	115.3	112.0
2.75	1.68	2.00	2.00	2.00	2.00	1.95	53.3	53.9	53.7	54.0	54.0	54.2
3.00	1.44	2.00	2.00	2.00	2.00	1.97	25.1	25.8	28.1	25.8	25.8	27.1
4.00	1.41	2.00	2.00	2.00	2.00	1.97	4.4	4.9	5.2	4.9	4.9	5.1
5.00	1.40	2.00	2.00	2.00	2.00	1.97	0.6	1.0	1.1	1.0	1.0	0.9
10.00	1.40	2.00	2.00	2.00	2.00	1.98	0.0	0.0	0.0	0.0	0.0	0.0

[a] Longer side of the H_4 rectangle, in bohr units. [b] Shorter side of the H_4 rectangle, in bohr units. [c] Fractional occupation number of the b_{2u} orbital. [d] Relative energy (in kcal/mol). [e] Exact occupation numbers and energies from ref 5. [f] This work. [g] DFT−FON results from ref 5. [h] Fractional occupation numbers of natural orbitals.

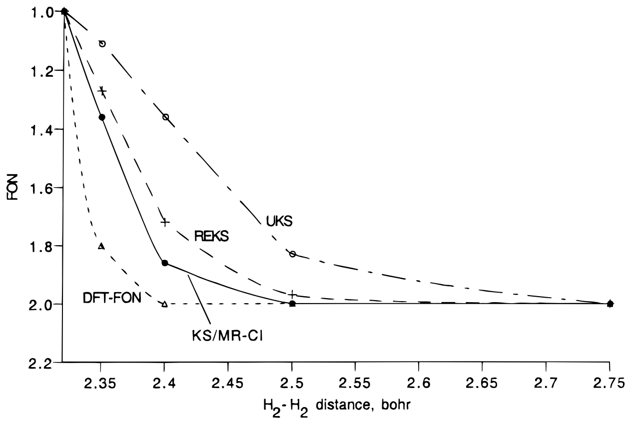


Figure 1. Fractional occupation numbers of the b_{2u} orbital obtained from an exact KS calculation (solid line), REKS/BLYP (long-dashed line), DFT-FON/BLYP (short-dashed line), and UKS/BLYP (dashed−dotted line) calculations.

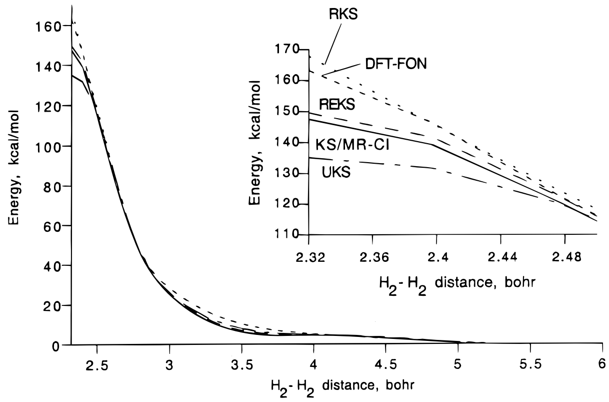


Figure 2. Potential energy surface for the $H_2 + H_2$ reaction obtained from MR−(S)DCI (solid line), REKS/BLYP (long-dashed line), RKS/BLYP (dotted line), DFT-FON/BLYP (short-dashed line), and UKS/BLYP (dashed−dotted line) calculations.

the same, e.g., with BP86.[50] The UKS method tends to overestimate the near-degeneracy correlation as manifested in a more rapid buildup of an ensemble than in the exact KS solution (see Figure 1). The DFT−FON method underestimates the nondynamic correlation, and the ensemble solution with this method starts to develop too late along the reaction coordinate.

Table 1 also presents the results of the (4,4)CASSCF calculations performed with the same cc-pV5Z basis set as in ref 5. Although the occupation numbers of the CASSCF natural orbitals cannot be regarded as the Kohn−Sham fractional occupation numbers,[29] we included the CASSCF results in the table (but not in Figures 1 and 2) to demonstrate that the conventional multireference ab initio treatment yields results parallel to the exact KS results given in the first column of Table 1.

An inspection of Figure 2, which presents the potential energy along the reaction coordinate, shows that the REKS method again yields results in closest agreement with the MR−(S)DCI calculations. Employing other density functionals may change the REKS energies slightly but qualitatively the picture remains the same. For example, the classical barrier height for this reaction from the REKS/BP86 calculation amounts to 146.4 kcal/mol and is again in closer agreement with the reference value of 147.5 kcal/mol than are the results from other methods.

The RKS method yields a cusp instead of a smooth curve at the high-symmetry point and overestimates the barrier height by as much as 20 kcal/mol. Note, however, that because we use a fairly sparse grid of points along the reaction coordinate, all curves look cusp-like; but in fact all methods except RKS yield smooth curves near the transition state. Although the DFT-FON method produces a smooth curve, the barrier height does not improve much in comparison with the RKS method.

The barrier height from the symmetry-broken UKS calculation is too low by more than 10 kcal/mol. This is a consequence of the erroneous spin-polarization in the UKS method that leads also to the overly fast development of the ensemble KS solution. As will be shown later, such an artifact may result in misleading predictions for the nature of active species in chemical reactions.

In summary, this example demonstrates that the REKS method yields a description of the near-degeneracy correlation effects that is most consistent with the exact KS results. Thus, even though we used a number of approximations in the development of the REKS method, the FONs of the KS orbitals obtained variationally with REKS are in the best agreement with the accurate values. Finally, one remark about the energies of the H_2 molecules which represent the "normal" state: at a distance of 10 bohr (reactants and products in the reaction considered), the REKS energy is −2.340567 hartrees and the RKS yields −2.340559 hartrees. Clearly, REKS converges to the usual KS solution for the "normal" situation.

Next, let us consider the rotation around the double bond in ethylene. In the ground state of the planar ethylene, the π orbital is doubly occupied and the π^* orbital is empty. As ethylene is twisted around the double bond, the energy gap between the bonding and antibonding π orbitals decreases and the orbitals become degenerate at 90° of twist. Therefore, in the vicinity of 90°-twisted ethylene, both densities, $(\pi)^2$ and $(\pi^*)^2$, contribute to the ground-state density.

Figure 3 shows potential energy curves along the twisting mode in ethylene calculated with the REKS, RKS, and UKS

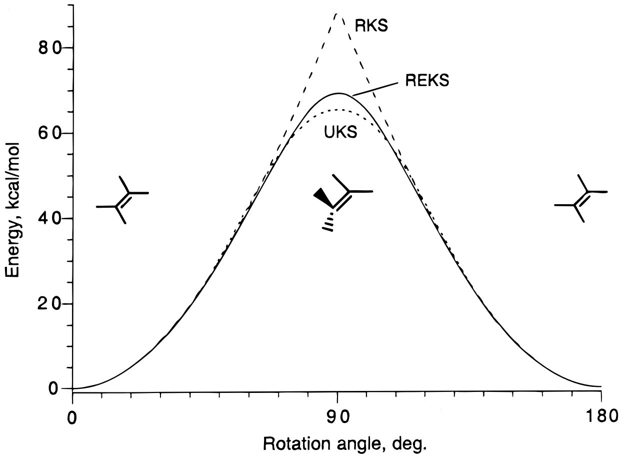


Figure 3. REKS/BLYP (solid line), RKS/BLYP (dashed line), and UKS/BLYP (dotted line) potential curves along the twisting mode in ethylene.

methods. The calculations employ the TZ2P basis set and BLYP density functional. The RKS calculation yields a sharp cusp at 90° of twist. Both of the other methods, UKS and REKS, yield smooth curves. The application of the conventional wave function methods to the twisting in ethylene is reviewed in ref 51, where it is demonstrated that only multireference methods can eliminate the cusp in the twisting curve.

As expected from the previous consideration, the UKS rotational barrier is lower than the REKS barrier. From Figure 3, the REKS barrier height is 69.1 kcal/mol and the UKS barrier is 65.3 kcal/mol. However, these values do not include the zero-point vibrational energies, and after correction for the ZPE (calculated with REKS and UKS employing the 6-31G* basis set), they become 66.4 and 60.9 kcal/mol from REKS and UKS, respectively. The REKS barrier is closer to the experimental value of 65 kcal/mol.[52] Although the numeric results of calculations may change with various density functionals, the trend remains that REKS yields higher barriers than UKS.

Both examples considered, the $H_2 + H_2$ reaction and ethylene twisting, involve high-symmetry transition states, where the degeneracy of both leading configurations is symmetry-dictated. Now, let us consider an avoided crossing where the degeneracy of leading configurations is accidental. One example of such a system is the tetramethyleneethane that we have studied previously[37] (that work is not repeated here). A second example is the [2.2.2]propellane (Figure 4) where the central C−C bond may acquire two different lengths.[3,53,54] In these bond-stretching isomers, the wave functions near the minima are pure closed-shell states.[3] In the short-bond-length isomer, the a_1' bonding orbital (shown in the left-hand-side inset) is doubly occupied, whereas in the long isomer the a_2'' antibonding orbital (shown in the right-hand inset) is filled. As the central C−C bond is stretched, the $(a_1')^2$ configuration is destabilized, and near the transition state it crosses with the $(a_2'')^2$ configuration; and this crossing gives rise to a strong nondynamic correlation.[3] It should be noted that in the D_{3h} symmetry retained along the central bond-stretching mode, both orbitals still belong to different irreducible representations at the crossing point, and their degeneracy is accidental.

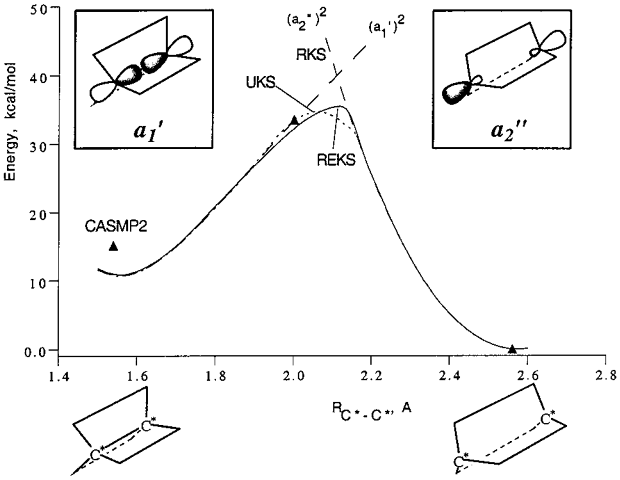


Figure 4. Potential energy profile along the isomerization mode in [2.2.2]propellane obtained from REKS/BLYP (solid line), RKS/BLYP (dashed line), UKS/BLYP (dotted line), and (8,8)CASMP2[54] (triangular markers) calculations. The a_1' and a_2'' orbitals are shown in the insets.

Figure 4 shows the potential curves along the bond-stretching mode in [2.2.2]propellane calculated with the REKS, RKS, and UKS methods. All calculations employ the 6-31G* basis set and the BLYP density functional and are subject to D_{3h} symmetry constraint. At each point along the curve, all geometric variables, with exception of the central C−C bond, were optimized. Again the RKS method is unable to provide a smooth connection between the minima, yielding two curves that correspond to the different configurations. The UKS and REKS methods yield smooth curves with nearly the same barrier height. The UKS method predicts an earlier transition state (at the C−C bond of 2.06 Å) than the REKS method (2.12 Å). This result is in line with our previous consideration that the ensemble solution in the UKS method develops earlier than in the REKS method. It is interesting to note that both density functional methods yield very close fractional occupation numbers of the a_1' and a_2'' orbitals at the transition point. The REKS method gives 1.62 and 0.38 and the UKS yields 1.63 and 0.37 for the a_1' and a_2'' orbitals, respectively.

The UKS and REKS potential energy profiles of propellane isomerization can be compared with the (8,8)CASMP2/6-31G* results.[54] The CASMP2 energies[54] of the respective minima and the transition state are shown by filled triangles in Figure 4. Both UKS and REKS barrier heights are in a reasonable agreement with the CASMP2 barrier. Again, as in the case of ethylene twisting, the REKS barrier is slightly higher than the UKS one. Unfortunately, we are not aware of any experimental data on this isomerization reaction,[54] and thus, we cannot determine which method performs better in this case.

(b) Diradicaloid Situations during Bond Dissociation. The inability of the single-reference methods to describe a homolytic bond dissociation is well-known.[55] The spin-unrestricted methods are able to yield the correct dissociation limit in bond-breaking processes, but at the price of symmetry breakage and heavy spin contamination.[14,56,57] These are the well-known facts, and we will consider homolytic bond-breaking briefly, giving two examples of such processes, H−H bond dissociation in H_2 and C−F bond dissociation in CH_3F. For these molecules, we calculated the dissociation curves using the REKS and RKS methods shown in Figures 5 and 6. The UKS curves, which in this case are qualitatively the same as the REKS curves, are not shown for brevity. Importantly, the REKS method provides the correct dissociation limit, but unlike UKS—which yields an incorrect spin density ($\langle \hat{S}^2 \rangle = 1$)—REKS leads to the correct spin situation. Furthermore, the REKS dissociation curves increase monotonically from the minimum to dissociation limit without the spurious maxima exhibited by some hybrid MR/DFT schemes at the intermediate distances.[10]

The ring-opening reactions discussed further represent an interesting example of bond-breaking processes. First, let us

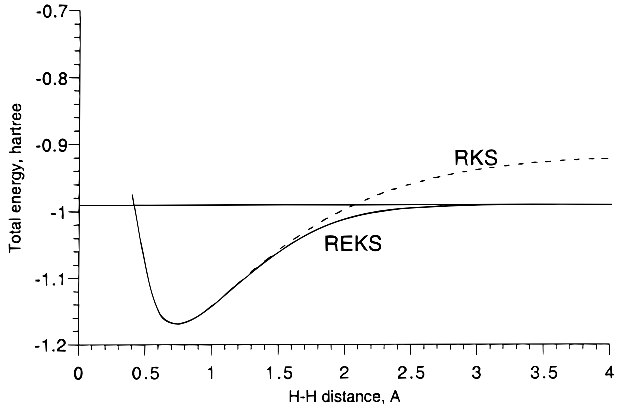


Figure 5. REKS/BLYP (solid line) and RKS/BLYP (dashed line) bond dissociation curves for H_2.

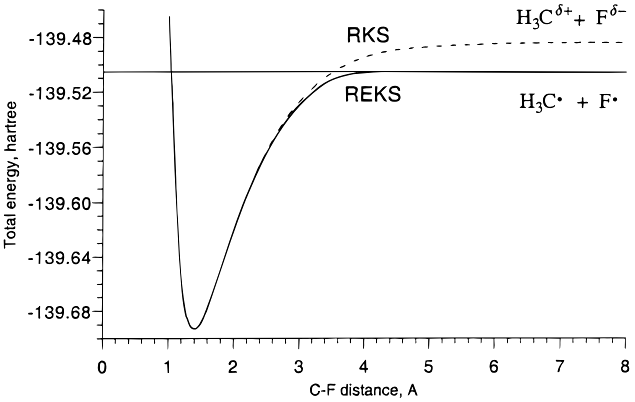


Figure 6. REKS/BLYP (solid line) and RKS/BLYP (dashed line) bond dissociation curves for the C−F bond in CH_3F.

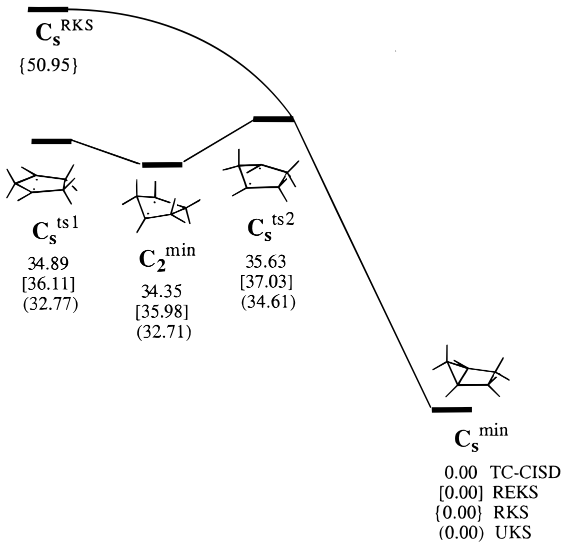
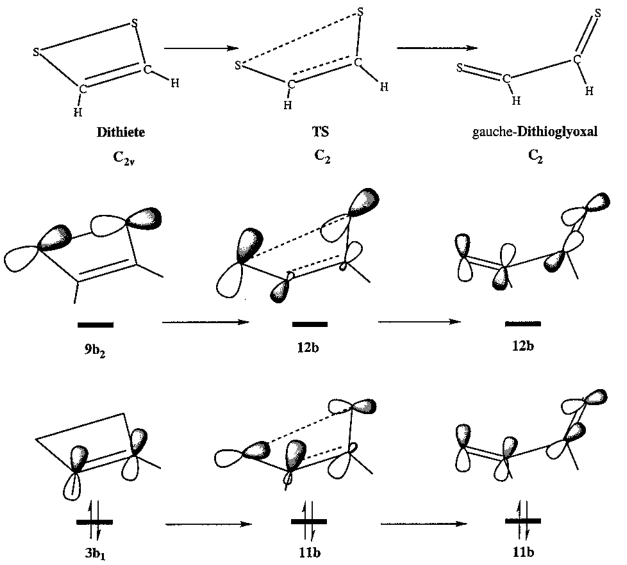


Figure 7. Potential energy profile of the isomerization between bicyclo[2.1.0]pentane and 1,3-cyclopentanediyl obtained from TC−CISD (without brackets), REKS/BLYP (in brackets), RKS/BLYP (in curly brackets), and UKS/BLYP (in parentheses) calculations.

SCHEME 2



consider the central C−C bond breaking in the bicyclo[2.1.0]pentane and its isomerization to 1,3-cyclopentanediyl (see Figure 7), also known as Closs's diradical.[58] This reaction has been extensively studied using the ab initio multireference methods.[59] CASSCF and TC−CISD calculations have established[59] that upon the breaking of the central C−C bond (Figure 7), a C_2-symmetric singlet diradical, C_2^{min}, is formed that is separated from the mirror image minimum by a C_s-symmetric transition state, C_s^{ts1}, and from the bicyclo[2.1.0]pentane by another C_s-symmetric transition state, C_s^{ts2}.

In the present work, employing the 6-31G* basis set and the BLYP density functional, we studied the potential surface of this reaction with the REKS, RKS, and UKS methods. Not surprisingly, RKS failed again and did not yield a local minimum corresponding to the C_2-symmetric singlet diradical. Instead, it yields a C_s-symmetric transition state that is characterized by a single imaginary frequency and is almost 15 kcal/mol too high compared to the corresponding TC−CISD energy (see Figure 7). This transition state and the two equivalent minima corresponding to bicyclo[2.1.0]pentane are the only stationary points on the RKS potential energy surface. The REKS and UKS calculations both successfully predict the existence of the C_2 local minimum and of both C_s transition states. Both methods place the C_2^{min} at approximately the same energy with respect to the bicyclo[2.1.0]pentane as TC−CISD. The REKS C_2^{min} is slightly above the TC−CISD energy and the UKS C_2^{min} is a little bit below it. The same trend is observed for the transition states C_s^{ts1} and C_s^{ts2}.

Thus, whereas for this reaction both the REKS and the UKS methods prove capable of describing quite delicate bond-breaking processes that cannot be described by single-reference methods, this is not the general situation. In certain situations, as a result of the unphysical spin-polarization in UKS and its pronounced preference to diradicaloid states, the UKS method fails and predicts wrong reaction mechanisms. Below we consider only one such failure, but numerous other examples exist.

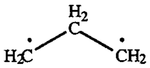
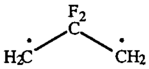
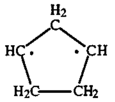
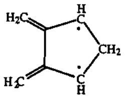
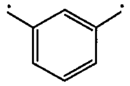
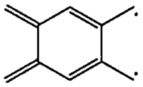
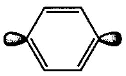
The ring-opening reaction of dithiete (Scheme 2) has been studied with the ab initio methods[60] and by use of symmetry-broken density functional calculations.[17] This reaction starts[17,60] with the planar C_{2v}-symmetric dithiete and terminates at the twisted C_2-symmetric gauche dithioglyoxal. Had this reaction proceeded via a C_{2v}-symmetric transition state, it would have been symmetry-forbidden. Along such a reaction mode the doubly filled $3b_1$ orbital would have been vacated and crossed with the $9b_2$ orbital, which itself is initially empty (see Scheme 2), thereby resulting in a diradicaloid transition state. However, in C_2 symmetry both orbitals belong to the same irreducible representation b. Consequently, in C_2 symmetry the reaction is no longer symmetry-forbidden and may proceed as shown in Scheme 2,[61] which may be rationalized in terms of the

TABLE 2: Energetic Parameters (in kcal/mol), Key Torsional Angles (in degrees), Occupation Numbers of Active Orbitals, and Total Spin in the Transition State for the Ring-Opening Reaction of Dithiete,[a]All Calculations Employ 6-31G* Basis Set

entry	method	$\Delta E^{\#}$	ΔE_{react}	∠SCCS[a]	∠HCCH[a]	n_{11b}	n_{12b}	S^2
1	REKS[b]	18.2	0.1	11.6	14.9	1.88	0.12	0.000
2	RKS[b]	18.7	0.1	13.8	17.3	2.00	0.00	0.000
3	UKS[b]	12.6	0.1	2.4	3.2	1.43	0.57	0.818
4	RHF	35.6	0.5	18.3	22.5	2.00	0.00	0.000
5	UHF	17.0	0.5	4.4	4.2	1.13	0.87	1.026
6	QCISD(T)	22.2	−2.4	15.5	18.4	2.00	0.00	0.000
7	(2,2)CASSCF	30.1	−6.2	14.9	19.3	1.89	0.11	0.000
8	(8,8)CASSCF[c]	16.9	0.8			1.91	0.16	0.000
9	(2,2)CASMP2[c]	16.3	−6.1					

[a] Refer to Scheme 2. [b] Calculations employ BLYP density functional. [c] Performed at (2,2)CASSCF geometries.

TABLE 3: Singlet−Triplet Energy Splitting in Diradicals Calculated by Use of REKS/BLYP, RKS/BLYP, and UKS/BLYP in Comparison with Available Experimental and Theoretical Data[a]

		ΔE_{ST}, kcal/mol				
Entry	Diradical	exp.	theor.	REKS	RKS	UKS
1			-0.7[b]	-0.8	-10.6	+0.40
2			+4.8[b]	+5.5	+0.4	+4.9
3		<0[c]	-1.19[c]	-2.12	-17.13	-0.52
4		<0[d]	-1.0[e]	-0.54	-8.46	+0.73
5		<0[f]	-10.0[g]	-12.46	-22.07	-9.09
6			+5.07[h]	+3.92	+1.44	+3.57
7		+3.8±0.5[i]	+4.7[j] +4.8[k] +5.5[l]	+4.89[m] +4.26[n]	-0.22[m] +1.02[n]	+4.07[m] +4.52[n]

[a] Calculations employ the 6-31G* basis set. The molecular geometries of the singlet and the triplet states are optimized. The zero-point vibrational corrections are not included unless noted otherwise. [b] From ref. 64. [c] From ref 59. [d] From ref 65. [e] From ref 66. [f] From ref 67. [g] From ref 68. [h] From ref 69. [i] From ref 70. [j] CASPT2 complete basis set limit from ref 71. [k] CASRS2 complete basis set limit from ref 71. [l] CCSD(T) from ref 63. [m] Values without ZPE. [n] Values with ZPE.

Woodward−Hoffmann rules.[62] The ab initio SCF and CASSCF methods predicted[60] for this reaction a C_2-symmetric transition state with pronounced twist of the C−S and C−H bonds around the central C−C bond. However, the symmetry-broken UKS calculations yielded[17] nearly planar transition structure with well-pronounced diradicaloid character. A conclusion has been drawn[17] that the reaction proceeds via the diradicaloid transition state.

To establish the preferred mechanism of this reaction, we undertook calculations with a number of the ab initio methods, ranging from single reference RHF, UHF, and QCISD(T) to multireference CASSCF and CASMP2 calculations (see Table 2). The molecular structures of critical species in this reaction have been optimized with the RHF, UHF, QCISD(T) and (2,2)CASSCF methods. As expected, all spin-restricted methods (RHF, QCISD(T), and (2,2)CASSCF) yield a twisted C_2-symmetric transition state. The key geometric parameters (entries 4, 6, 7 in Table 2) are close to each other. It is interesting that the (2,2)CASSCF does not predict any significant diradicaloid character for the transition state, although both important orbitals have been included into the active space. Furthermore, the (8,8)CASSCF calculation (entry 8) does not much change the occupation numbers of the corresponding natural orbitals. The barrier height from the high-level ab initio calculations ranges from 22.2 kcal/mol with QCISD(T) to 16.3 kcal/mol with CASMP2.

The UHF method leads to a completely different picture. The transition structure is nearly planar with nearly equal occupation numbers of the natural orbitals 11b and 12b, which indicate a pronounced diradicaloid character of the transition state. Due to heavy spin contamination, the activation barrier is too low compared to other low-level ab initio methods (entries 4 and 7).

The application of density functional methods to this reaction revealed that REKS/BLYP and RKS/BLYP both yield essentially nonplanar transition structure with geometric parameters close to the ab initio ones (see entries 1 and 2 in Table 2). The REKS method provides a solution which is represented by an ensemble with occupation numbers 1.88 and 0.12. These occupation numbers of the active orbitals are nearly the same as in the best multireference ab initio calculation. These occupation numbers (Table 2) clearly indicate a quite moderate nondynamic correlation in the transition state. This is perhaps why the RKS barrier is close to the values obtained by REKS, and (8,8)CASSCF or CASMP2.

The UKS/BLYP calculation (entry 3 in Table 2), like the UHF, predicts nearly planar transition state with a pronounced diradicaloid character and a very low barrier. Thus, consistent with our previous observations, the UKS method overemphasizes the ensemble character in the KS solution. It should also be noted that with pure density functionals, such as the BLYP functional, the diradicaloid character of the transition state is smaller than from the UHF calculation. However, the use of the hybrid HF/DFT functionals, such as B3LYP and B3PW91, restores[17] nearly the same diradical picture as in UHF. Consequently, the UKS and UHF methods predict for this reaction a diradicaloid mechanism, which is in contrast with the high-level ab initio methods which show very small diradicaloid character. In conclusion, REKS provides an adequate description of the nondynamic correlation effects in this reaction, as opposed to the UKS method.

(c) State Ordering in Diradicals. The singlet−triplet (S−T) energy splitting may indicate the performance of the computational scheme used in the study of diradicals.[63] The standard single-reference RKS method fails to describe the S−T splitting in diradicals correctly. The symmetry-broken UKS method often provides good results for S−T splittings at the expense of an ill-described singlet diradical with a spin-density different than zero. Table 3 summarizes the results of our calculations of S−T splittings (negative sign indicates the triplet ground state) for a number of diradicals with the REKS, RKS, and UKS methods in the 6-31G* basis set. In some cases the sign of S−T splitting as well as its numeric value have been determined experimentally. In all the cases in the table, the results of multireference ab initio calculations of S−T splittings are available from literature.

Indeed, as may be seen, RKS does not perform well for the S−T splittings. Both other methods, UKS and REKS, yield numerically reasonable S−T gaps. However, closer inspection of the data in Table 3 reveals that UKS is biased toward singlet states. In certain cases (entries 1 and 4 in Table 3), UKS incorrectly predicts a singlet ground state of diradicals. This implies that, especially in case of the small S−T gaps, the results of symmetry-broken UKS calculations should be accepted with caution. In contrast, the REKS method uniformly predicts the correct ground state and numerically good S−T gaps for all the diradicals in the table.

V. Conclusions

We have presented a simple yet effective KS-type computational scheme capable of treating systems with strong nondynamic correlation. The computational scheme of REKS is based on the ensemble representation of the density and energy for strongly correlated systems, in terms of densities and energies of several single KS determinants. The ensemble representation results in the appearance of the fractional occupation numbers of the KS orbitals. An optimal set of orthonormal KS orbitals and their occupation numbers are obtained in the REKS method variationally by minimization of the ground-state energy with respect to the density.

The benchmark calculations reported in the present paper show the effectiveness of the new approach. Thus, the REKS method yields the description of the near-degeneracy correlation effects that is most consistent with KS results derived from exact densities[5] and with the ab initio multireference results. In addition to these properties, the REKS method is free of the spin contamination that is inherent in symmetry-broken, spin-unrestricted methods, and also of the double-counting of the correlation energy that seems to occur in hybrid MR/DFT computational schemes.[9] Retaining simplicity of the usual KS calculation, the REKS method can yield, at least for the test systems, results of essentially the same quality as conventional multireference methods such as CASPT2 and MR−(S)DCI.

The REKS method can easily be implemented in the existing quantum-chemical packages and can work with any existing density functional, be it a hybrid HF/DFT or a pure density functional. Although we used the BLYP pure density functional, the results of REKS calculations remain qualitatively the same with any other density functional; only the numerical value may change. The described version of the REKS method applies to situations in which two electrons are delocalized in two degenerate or nearly degenerate orbitals, as occurs in diradicals. By analogy with CASSCF the method may be termed REKS(2,2) (i.e., two active electrons in two active KS orbitals). Extensions of the REKS method to situations with three and four active electrons and orbitals are already available and will be presented elsewhere.[38]

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